

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 December 2001 (06.12.2001)

PCT

(10) International Publication Number
WO 01/92439 A1

(51) International Patent Classification⁷: **C10G 53/12**,
27/02

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(21) International Application Number: **PCT/GB01/02205**

(22) International Filing Date: **17 May 2001 (17.05.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
0013086.4 **30 May 2000 (30.05.2000)** **GB**

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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WO 01/92439 A1

(54) Title: **PROCESS FOR REMOVING METAL IONS FROM CRUDE OIL.**

(57) Abstract: A process for removing metal ions from crude oil comprising contacting a non-ionic amphiphilic solvent with the crude oil, optionally, in the presence of water, so as to produce a metal ion-containing phase, and separating the metal ion-containing phase from the crude oil.

Process for Removing Metal Ions from Crude Oil

The present invention relates to a process for removing metal ions from crude oil.

Crude oil and its distillates often contain metal ion impurities. Such impurities include metal ions from Group IA and IIA of the Periodic Table, such as sodium, potassium, calcium and magnesium. These impurities often find their way into the oil when the oil is deacidified, as metal oxides, hydroxides and/or carbonates are routinely employed as neutralising agents.

Metal ions in the oil can cause fouling problems, particularly, in refinery operations. This is because in such operations, high temperatures in excess of 200°C are encountered, causing the metals to deposit on the refinery equipment. For this reason, it is desirable to remove metal ions from the oil.

WO 98/14402 describes a process for removing +2 ionic charged metals from a petroleum feed. The process involves contacting the feed with a resin that includes carboxyl, sulphonic and/or phosphonic groups.

It has now been found that metal ions can be removed from crude oil using a non-ionic amphiphilic solvent.

Accordingly, the present invention provides a process for removing metal ions from crude oil comprising

contacting a non-ionic amphiphilic solvent with the crude oil, optionally, in the presence of water, so as to produce a metal ion-containing phase, and

separating the metal ion-containing phase from the crude oil.

Preferably, the contacting step is carried out in the presence of water.

The term "crude oil" above is intended to cover whole crudes as well as crude oil

distillates. Preferably, however, the process is carried out on whole crude oils.

The non-ionic amphiphilic solvent may be an alcohol. Preferably, the solvent is a polyol, such as an alkyltriglycol ether. The alkyl group of the alkyltriglycol ether may be straight or branched chain and suitably has 3-6 carbon atoms, preferably 3-5 carbon atoms. More preferably, the alkyl group in the alkyltriglycol ether has 4 carbon atoms and is especially n-butyltriglycol ether (also known as triethylene glycol mono-n-butyl ether). Other suitable glycol ethers include ethylene glycol mono ethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-iso-butyl ether, ethylene glycol mono-2-butyl ether, ethylene glycol mono-tert-butyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-iso-propyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-iso-butyl ether, diethylene glycol mono-2-butyl ether, diethylene glycol mono-tert-butyl ether, diethylene glycol mono-n-pentyl ether, diethylene glycol mono-2-methylbutyl ether, diethylene glycol mono-3-methyl butyl ether, diethylene glycol mono-2-pentyl ether, diethylene glycol mono-3-pentyl ether, diethylene glycol mono-tert-pentyl ether, tetraethylene glycol mono butyl ether and pentaethylene glycol mono butyl ether. Mixtures of solvents may also be employed. Such mixtures may be more robust than their individual components. Thus, n-butyltriglycol ether may be used in combination with n-butyldiglycol ether, n-butyl tetraglycol ether and n-butyl pentaglycol ether. In one embodiment of the invention, the solvent comprises 75 w/w% n-butyltriglycol ether, 2.5 w/w% n-butyldiglycol ether, 19.0 w/w% n-butyl tetraglycol ether and 2.0w/w% n-butyl pentaglycol ether.

Without wishing to be bound by any theory, it is believed that the non-ionic amphiphilic solvent has a large capacity to solubilise or dissolve metal ions. When the crude oil is contacted with the non-ionic amphiphilic solvent in the absence of water, the metal ions in the crude oil partition into the non-ionic amphiphilic solvent (which is immiscible with the crude oil). The resulting non-ionic amphiphilic solvent phase is thus a metal ion-containing phase, which is subsequently separated from the crude oil. This separation step may be carried out using a density separator, for example, a decanter or hydrocyclone.

Where the contacting step is carried out in the presence of water, the non-ionic amphiphilic solvent is believed to couple the oil and water together forming a middle

phase having a density intermediate between that of oil and water. This is believed to be possible because of the miscibility gap between the water and crude oil. The middle phase exhibits low interfacial tension between the oil and water, and has a large capacity to solubilise or dissolve metal ions. The middle phase is thus a metal ion-containing phase. The crude oil may subsequently be separated from the middle phase (metal ion-containing phase) and water using a density separator, for example, a decanter or hydrocyclone.

With certain non-ionic amphiphilic solvents, the middle phase may not appear in the presence of water, until the reaction mixture is heated above a threshold temperature. With n-butyltriglycol ether, for example, the middle phase does not become apparent until the crude oil/water/solvent mixture is heated to approximately 70°C. Below this temperature, the non-ionic amphiphilic solvent is substantially miscible with water. This non-ionic amphiphilic solvent/water mixture may nevertheless have the capacity to dissolve metal ions. Thus, instead of becoming suspended in the middle phase as described above, the metal ions in the crude oil may become suspended in the non-ionic amphiphilic solvent/water phase. This solvent/water phase is a metal-containing phase, which may be separated from the crude oil directly. Preferably, however, the crude oil/water/solvent system may be heated to at least 70°C, so as to produce the middle phase. This middle phase is the metal-ion containing phase, which is subsequently separated.

It should be understood that the threshold temperature may vary depending on the nature of the non-ionic amphiphilic solvent employed. It may be possible to lower this threshold temperature by using mixtures of two or more solvents.

In certain cases, it may be desirable to treat the metal-containing phase, so as to separate the metal ions from the non-ionic amphiphilic solvent. This allows the non-ionic amphiphilic solvent to be recycled for reuse. Metal ions may be separated from the non-ionic amphiphilic solvent by distilling off the solvent. Alternatively, the metal ions may be removed from the non-ionic amphiphilic solvent using a membrane or an ion-exchange column. It may also be possible to separate the metal ions by using another solvent extraction step.

The crude oil may be contacted with the non-ionic amphiphilic solvent at a temperature of up to 160°C. Preferably, the crude oil is contacted with the non-ionic

amphiphilic solvent at a temperature above the threshold temperature. However, where the contact temperature is not sufficiently high for the middle phase to appear, it is desirable to heat the resulting mixture to effect the appearance of this middle phase.

The contact temperature may range between ambient temperature and 160°C,

5 preferably, between 70 and 160°C, more preferably, between 80 and 125°C, and most preferably, between 80 and 100°C. If a temperature of above 100°C is employed, it may be desirable to operate the process at elevated pressure, for example at 5 to 20 bar.

As mentioned above, the non-ionic amphiphilic solvent is preferably contacted with the crude oil in the presence of water. The crude oil may contain some formation, connate, injection, aquifer and/or nascent water. Preferably, however, at least some of
10 the water present during the contacting step is added to the crude oil. Addition of fresh water is advantageous since this will lower the salinity of the aqueous phase, thereby lowering the threshold temperature. It is particularly advantageous to use the non-ionic amphiphilic solvent as an aqueous solution. The concentration of non-ionic amphiphilic
15 solvent in water may be between 8 and 70 w/w%, preferably, between 15 and 60 w/w%.

The amount of non-ionic amphiphilic solvent employed may form 5 to 40, preferably, 10 to 30 wt% of the total amount of oil, amphiphilic solvent and optional water in the reaction mixture. Where water is present, it may 5 to 40, preferably, 10 to
20 30 wt% of the reaction mixture.

Once the non-ionic amphiphilic solvent is contacted with the oil, the resulting mixture may be stirred or agitated in a mixing unit. The mixture may be stirred using a mechanical stirrer, an ultrasonic stirrer or by bubbling an inert gas through the reaction mixture. The mixing step may last 2 to 30 minutes, preferably, 5 to 20 minutes and most preferably, 8 to 15 minutes. The mixing step may be carried out at a temperature
25 of 5 to 160°C, preferably 10 to 70°C, most preferably, 20 to 50°C, and especially 30 to 40°C. Where the non-ionic amphiphilic solvent is contacted with the crude oil in the presence of water, the reaction mixture is then preferably heated to above the threshold temperature.

In certain embodiments of the invention, it may be desirable to contact the crude
30 oil with the non-ionic amphiphilic solvent in the presence of an organic diluent, such as decane, gasoline, gas oil, diesel or kerosene.

The process of the present invention may be used to remove any metal ions,

including those in Groups IA and IIA of the Periodic Table from crude oil. Specific examples of metal ions include sodium, potassium, magnesium, and in particular, calcium. These metal ions may be present in any form, for example, as naphthenate, chloride, phenolate and/or sulphate salts. These salts may be formed when neutralising agents such as metal hydroxides, oxides and/or carbonates are contacted with the crude oil. Accordingly, the process of the present invention provides a convenient method of removing the salts produced when deacidifying crude oil from crude oil.

Thus, a further aspect of the present invention provides a process for reducing the acidity of crude oil comprising

10 contacting crude oil with i) a metal-containing neutralising agent in the presence of water and ii) a non-ionic amphiphilic solvent with the crude oil.

The non-ionic amphiphilic solvent employed may be contacted with the crude oil before, after or at the same time as the metal-containing neutralising agent. Preferably, the non-ionic amphiphilic solvent is contacted with the oil after the metal-containing neutralising agent. Suitable non-ionic amphiphilic solvents have been described in relation to the first aspect of the present invention. As described above, the non-ionic amphiphilic solvent draws metal ions from the crude oil into a metal ion-containing phase: this metal-ion containing phase may subsequently be separated from the crude oil.

20 The metal containing neutralising agent is suitably a metal hydroxide, oxide or carbonate. Group IA and IIA hydroxides and oxides, for example, those of sodium, potassium, barium, calcium and magnesium are preferred. Of these, hydroxides of sodium potassium and in particular, calcium are most preferred. These hydroxides neutralise acids, such as naphthenic acids, which are present in crude oil, producing water and neutralisation salts eg metal naphthenates.

25 The concentration of water present in the neutralisation step may be 0.01 to 100 wt % of oil. Water is believed to aid the neutralisation reaction by catalysing the transfer of hydrogen ions between the oil and neutralising agent. For these reasons, water may have to be added to the reaction mixture. Some crude oils, however, may themselves contain sufficient water to aid the transfer of hydrogen ions. In such cases, the addition of water may not be necessary.

Water is also produced during the deacidification reaction. Thus, the water

concentration increases during the process of the present invention. For water to be generated in this manner, however, at least some traces of water must be initially present.

Preferably, water concentrations of 0.01 to 30, more preferably 0.01 to 25 wt %, even more preferably, 0.1 to 20 wt %, most preferably, 3 to 20 wt %, and especially 10 to 15 wt % are employed during the deacidification step.

Where the non-ionic amphiphilic solvent is contacted with the crude oil after neutralisation, it may be desirable to remove some or substantially all of the water dispersed in the crude oil phase before the solvent is added, to ensure that the amphiphilic solvent is not diluted or is not diluted to too high a degree. One way of removing the water is to use a demulsifier. The demulsifier may cause the crude oil/neutralising agent mixture to separate into three phases: an oil-rich phase, an aqueous phase and an interface or "ragging" layer, disposed between the oil-rich and aqueous phases. The non-ionic amphiphilic solvent may be added directly to this three-phase mixture. Alternatively, the oil-rich phase may first be recovered from the three-phase mixture. The non-ionic amphiphilic solvent may then be added to the recovered oil-rich phase, preferably in the presence of water.

Any demulsifier suitable for breaking water-in-oil type emulsions may be employed. Suitably the demulsifier comprises at least one surfactant selected from the group consisting of:

(a) polyamine salts such as polyester amines, amino methylated poly acrylamide, poly di-methyl amino propyl methacrylamide, poly dimethyl amino ethyl acrylate, poly ethylene imine, poly vinyl pyrrolidone, caprolactam-based polymers and quaternised versions of the above. Suitably, the molecular weight of the polyamine salt is above 3000;

(b) multifunctional polyethers such as sulfated triglycerides;

(c) polyethers, such as copolymers of ethylene oxide and propylene oxide and the reaction products of such copolymers with diacids, diepoxides, diisocyanates, aldehydes, and diamines. Suitably, the molecular weight of the polyether is above 2000; and

(d) p-alkylphenol-formaldehyde resins and ethylene oxide and/or propylene oxide derivatives thereof.

Suitably, the demulsifier comprises a solution of the surfactant(s) dissolved in a solvent such as monoethylene glycol (MEG), tetraethylene glycol (TEG), butylethylene glycol (BGE), butyldiethylene glycol (BDGE), water, xylene and toluene.

Suitable demulsifiers may also be prepared by reacting I) an addition product of
5 a phenol and formaldehyde or acetaldehyde, with II) a block polymer containing nitrogen. Preferably, the mole ratio of I to II is 1 - 20 : 1.

The addition product.(I) may be obtained by reacting phenol with formaldehyde or acetaldehyde in a molar ratio of 1:1 to 3, preferably 1:1.8 to 2.2 at a temperature of 50° to 80°C, in the presence of an alkaline catalyst. The block polymer (II) may be
10 obtained by an addition reaction between ethylene oxide, propylene oxide and ethylenediamine, propylenediamine, polyethylenepolyamines, polypropylenepolyamines or mixtures thereof. Preferably, 10 to 80 moles, more preferably, 30 to 70 moles, of ethylene oxide and propylene oxide are added, as a statistical average per nitrogen atom. Typically, the molar ratio of ethylene oxide to
15 propylene oxide is 1:0.5 to 14, preferably, 1:1 to 8. Suitable demulsifiers are described in US 4 474 682.

A preferred demulsifier is ML 3407TM (supplied by Baker Petrolite).

The concentration of demulsifier employed may be 0.01 to 5 wt %, preferably, 0.1 to 2 wt % and especially 0.1 to 0.5 wt % of oil.

20 The process of the present invention may be carried out on a refinery, or whilst the oil is being transported, for example, in a tanker at sea.

Example

In this example, 600 ml of crude oil containing 300 - 400ppm Ca was contacted with 150g of a non-ionic amphiphilic solvent consisting of 75 w/w% n-butyltriglycol
25 ether, 2.5 w/w% n-butyldiglycol ether, 19.0 w/w% n-butyl tetraglycol ether and 2.0w/w% n-butyl pentaglycol ether. The contacting step was carried out in the presence of 150 g of salt (?) water. The reaction mixture was then heated to approximately 70°C. This caused the reaction mixture to separate into three phases: an oil-rich phase, an aqueous phase and a middle phase disposed between the aqueous and oil-rich phases.

30 The oil-rich phase was recovered from this 3 phase mixture and found to have a Ca ion concentration of approximately 9 ppm. This showed that Ca ions originally present in the crude oil were removed by the addition of the non-ionic amphiphilic

solvent.

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Claims

1. A process for removing metal ions from crude oil comprising
 - a) contacting a non-ionic amphiphilic solvent with the crude oil, optionally, in the presence of water, so as to produce a metal ion-containing phase, and
 - b) separating the metal ion-containing phase from the crude oil.
- 5 2. A process as claimed in claim 1, wherein step a) is carried out in the presence of water.
3. A process as claimed in claim 1 or 2, wherein the non-ionic amphiphilic solvent comprises an alcohol or an alcohol derivative.
4. A process as claimed in claim 3, wherein said solvent comprises a polyol.
- 10 5. A process as claimed in claim 3, wherein said solvent comprises an alkyltriglycol ether.
6. A process as claimed in claim 3, wherein said solvent comprises at least one compound selected from the group consisting of n-butyltriglycol ether, ethylene glycol mono ethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-
15 propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-iso-butyl ether, ethylene glycol mono-2-butyl ether, ethylene glycol mono-tert-butyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-iso-propyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-iso-butyl ether, diethylene glycol mono-2-butyl ether, diethylene glycol mono-tert-butyl ether, diethylene glycol mono-n-pentyl
20 ether, diethylene glycol mono-2-methylbutyl ether, diethylene glycol mono-3-methyl butyl ether, diethylene glycol mono-2-pentyl ether, diethylene glycol mono-3-pentyl ether, diethylene glycol mono-tert-pentyl ether, tetraethylene glycol mono butyl ether,

and pentaethylene glycol mono butyl ether.

7. A process as claimed in claim 6, wherein said solvent is a mixture of n-butyltriglycol ether, n-butyldiglycol ether, n-butyl tetraglycol ether and n-butyl pentaglycol ether.
- 5 8. A process as claimed in claim 7, wherein said mixture comprises 75 w/w% n-butyltriglycol ether, 2.5 w/w% n-butyldiglycol ether, 19.0 w/w% n-butyl tetraglycol ether and 2.0w/w% n-butyl pentaglycol ether.
9. A process as claimed in any preceding claim, wherein the metal ion-containing phase is separated from the crude oil using a density separator.
- 10 10. A process as claimed in any preceding claim, wherein prior to separating the metal ion-containing phase from the crude oil, the reaction mixture of step a) is heated to at least 70 °C.
11. A process as claimed in any preceding claim, which further comprises the step of recovering at least some of the non-ionic amphiphilic solvent from the metal-containing
15 phase separated in step b) for re-use.
12. A process as claimed in claim 11, wherein the non-ionic amphiphilic solvent is recovered from the metal-containing phase by distillation, a membrane, an ion-exchange column and/or an additional solvent extraction step.
13. A process as claimed in any preceding claim, wherein step a) is carried out at
20 between ambient temperature and 160°C.
14. A process as claimed in any one of claims 2 to 13, wherein the non-ionic amphiphilic solvent is contacted with the crude oil as an 8 to 70 w/w% aqueous solution of the solvent.
15. A process as claimed in any preceding claim, wherein the amount of non-ionic
25 amphiphilic solvent employed forms 5 to 40 wt% of the total amount of oil, amphiphilic solvent and optional water in the reaction mixture of step a).
16. A process for reducing the acidity of crude oil, comprising contacting crude oil with
 - i) a metal-containing neutralising agent in the presence of water, and
 - 30 ii) a non-ionic amphiphilic solvent, so as to produce a metal-containing phase, and optionally, separating the metal-containing phase from the crude oil.
17. A process as claimed in claim 16, wherein the metal containing neutralising agent

is a hydroxide, oxide and/or carbonate of a Group IA and/or Group IIA metal.

18. A process as claimed in claim 17, wherein the metal containing neutralising agent is calcium hydroxide.

19. A process as claimed in any one of claims 16 to 18, wherein the non-ionic
5 amphiphilic solvent employed is contacted with the crude oil before, after or at the same time as the metal-containing neutralising agent.

20. A process as claimed in claim 19, wherein the non-ionic amphiphilic solvent is contacted with the oil after the metal-containing neutralising agent is contacted with the crude oil.

10 21. A process as claimed in any one of claims 16 to 20, wherein a demulsifier is added to the reaction mixture of step i), prior to the addition of the non-amphiphilic solvent of step ii).

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/02205

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G53/12 C10G27/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 00 75262 A (COLLINS IAN RALPH ;DUNCUM SIMON NEIL (GB); BP EXPLORATION OPERATIN) 14 December 2000 (2000-12-14) claims 1-11	1-21
A	WO 98 14402 A (EXXON RESEARCH ENGINEERING CO) 9 April 1998 (1998-04-09) cited in the application the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

14 August 2001

Date of mailing of the international search report

21/08/2001

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/02205

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